# APPLICATION OF NEW INSTRUMENTAL METHODS TO THE STRUCTURAL PROPERTIES OF LIMES, MAGNESIA, AND BORDEAUX SPRAYS

BY

JOHN P. TORDELLA

B. S., Loyola University, 1941

M. S., University of Illinois, 1942

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS

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# PART I

## STRUCTURAL PROPERTIES OF LIME

### Introduction

One of the criteria of a good plastering lime is good plasticity, that is, the plaster must apply to the wall easily without pull or sag. Many studies have been made of this structural property. Particle size, shape and activity have been evaluated by sedimentation methods and by x-ray diffraction, and correlated to plasticity values. Two theories have been proposed to explain the fundamental reasons for variation in plasticity. Bonnell[1] concluded from sedimentation studies that plasticity is an inverse function of the tendency of small primary particles to agglomerate. Bernays,[2] working in x-ray diffraction found that plasticity is related to particle size and shape. Thin flat plate-like particles, of an order of size of a hundredth of a micron, were found in limes of high plasticity and equiaxed particles were found in limes of low plasticity.

This investigation was conducted in order to provide more information about plasticity. Optical and electron microscopy were employed to study particle size, shape, and agglomeration. Methods of evaluating activity of limes were devised in order to secure more information about plasticity.

### Experimental Results

In the range of the magnification of the optical microscope various samples appear quite similar. The electron microscope on the other hand, proved very useful, and indicated a correlation between the two diverse theories of plasticity. Samples of high plasticity were seen to be large loose agglomerates of primary particles, which were about a hundredth of a micron in size. The primary particles of less plastic samples appeared to be fewer in number and somewhat larger and thicker. The agglomerates of these samples were

tough and angular. The primary particles were about the size of the particles evaluated by x-ray diffraction and, the properties of these particles seemed to determine the degree and manner of agglomeration.

In order to study the activity of various limes calorametric determination of the heats of wetting, the rate of hydration of magnesium oxide in dolomitic hydrates, adsorption of methylene blue from solution, and chromatographic adsorption were studied. Heats of wetting were small and erratic. The rates of hydration of magnesium oxide, determined by x-ray diffraction analysis were quite similar, but another effect was noted, preferential grain growth. The grains in the more active sample grew more rapidly than those in the less active sample. This method, though time consuming and difficult to evaluate, is positive. Methylene blue adsorption was similar for all samples. The most promising method, use of chromatographic analysis to study the adsorption, was not worked out successfully.

## PART II

## THE STRUCTURAL PROPERTIES OF MAGNESIA

### Introduction

The Lime industry is turning to new fields. Magnesium metal produced from dolomite is a recent product. Magnesium oxides are now being made from the same raw material. This study was an attempt to correlate the following properties of six samples: apparent density, particle size evaluated by x-ray diffraction, catalytic activity, and particle size and shape as seen in the electron microscope. The samples differed slightly in the method of preparation.

Most of the previous work on magnesium oxides has been limited to the study of methods of production of refractory and catalytic oxides. Bussem[3] used x-ray diffraction to study active oxides and found very small, distorted particles.

### Experimental Results

The apparent densities which were determined by weighing about a cubic foot of the bulk material varied considerably. A factor of almost five existed between the most and the least dense samples. The densities were eight to thirty-seven times smaller than that of natural periclase.

X-ray diffraction analysis indicated roughly similar particle sizes, about ten to the minus sixth or seventh centimeters.

Catalytic activity was determined by measuring the oxygen evolved from the decomposition of hydrogen peroxide. With one exception, the activity of the samples increases in order of decreasing density. The odd sample was less active than its density would indicate and differed in that it was calcined over a bunsen burner rather than in an electric muffle.

The electron microscope pictures, magnification 21,000x, showed a large difference in the manner of agglomeration of the small primary particles. These small particles are the ones evaluated in x-ray diffraction analysis. The most active samples were composed of small, very thin, poorly formed agglomerates. As the activity of the samples decreased thicker and more perfectly formed flakes and needles appeared. The electron microscope proved to be a valuable tool in understanding the causes of variations in density, and activity of the various samples of magnesia.

## PART III

## STRUCTURAL PROPERTIES OF BORDEAUX SPRAYS

### Introduction

The diversity of opinion regarding the desirability of using dolomitic and high calcium limes interchangeably in the preparation of Bordeau sprays led to this x-ray diffraction study of the compounds present in these sprays.

Since Pickering's[4] work in 1888, many people have studied

the compounds formed when a copper sulfate solution is made basic. Binder[5] gives a good resume of this work. It is generally agreed that one compound, $CuSO_4 \cdot 3CuO$, exists. There is controversy regarding the exact number and nature of compounds more basic than this. In this study no attempt was made to determine the formulae of the various compounds formed by the four bases, sodium hydroxide, high calcium hydrate, a dolomitic hydrate containing thirty-six percent magnesium oxide, and magnesium oxide.

## Experimental Results

Debye-Sherrer patterns of precipitates formed by action of all four bases showed identical compounds, which did not correspond to any of the compounds which might be present, other than basic copper sulfate. Thus it was concluded that the patterns of all basic copper sulfates formed in Bordeaux sprays may be compared without regard to the presence of other products.

Patterns were made of precipitates of four Bordeaux sprays containing equivalently four pounds of $CuSO_4$, three pounds of lime, and fifty gallons of $H_2O$. Two of these sprays were made with high calcium lime, and two with dolomitic lime. The patterns of the samples made with the same lime differed slightly in both cases. This indicated that basic copper sulfates are of indefinite composition. A somewhat larger characteristic difference existed between the patterns of dolomitic and high calcium Bordeaux. Since the compounds formed vary, differences between Bordeaux made with high calcium and dolomitic lime are not considered as serious as if individual and different compounds were always formed.

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## Vita

The Author was born May 24, 1919, in Garrett, Indiana. He received primary, secondary, and undergraduate education in Chicago. After graduation in 1937 from Saint Ignatius High School, he entered Loyola University and graduated with a Bachelor of Science degree, cursu ad honores peracto, in June 1941. He was enrolled in the Graduate School of the University of Illinois in September, 1941 and held for three years a Special Research Assistantship sponsored by the National Lime Association.

He is a member of Delta Epsilon Sigma, Sigma Xi, and the American Chemical Society.

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